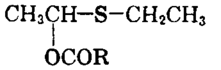
This work has now been extended to include thioethers.[2]

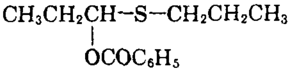
It is well known that sulfides react with various peroxy compounds such as hydrogen peroxide, peracids,[3] and hydroperoxides[4] to give good yields of sulfoxides or sulfones. In contrast, we have found that *t*-butyl peresters react smoothly with aliphatic and cyclic sulfides to give the corresponding acyloxy derivatives and that there is no oxidation of the sulfur atom under the chosen experimental conditions.

Specifically, the reaction of 0.3 mole of *t*-butyl peracetate with 0.35 mole of diethyl sulfide in benzene (50 ml.) in the presence of 0.35 mmole of cuprous bromide for 64 hr. at 80–85° yielded 44% of 1-acetoxy diethyl sulfide (Ia), b.p. 70–72°, 22 mm., n_D^{25} 1.4468, $\gamma_{C=O}$ 1730 cm.$^{-1}$ *Anal.* Calcd. for $C_6H_{12}O_2S$: C, 48.64; H, 8.16, S, 21.60; mol. wt., 148. Found: C, 48.84; H, 8.30; S, 21.97; mol. wt., 146.



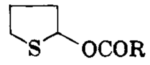
$CH_3\underset{OCOR}{CH}-S-CH_2CH_3$

Ia. R=CH_3
Ib. R=C_6H_5



$CH_3CH_2\underset{OCOC_6H_5}{CH}-S-CH_2CH_2CH_3$

II



IIIa. R=CH_3
IIIb. R=C_6H_5

Similarly, the reaction of 0.2 mole of *t*-butyl perbenzoate and 0.5 mole of diethyl sulfide in the presence of 0.35 mmole of cuprous bromide for 26 hr. at 80–90° yielded 31% of Ib, b.p. 75° at 0.1 mm., n_D^{25} 1.5266, $\gamma_{C=O}$ 1715 cm.$^{-1}$ *Anal.* Calcd. for $C_{11}H_{14}O_2S$: C, 62.84; H, 6.71; S, 15.22; mol. wt., 210. Found: C, 63.40; H, 6.98; S, 15.03; mol. wt., 216.

Under similar catalytic conditions, 0.4 mole of *t*-butyl perbenzoate reacted with 0.4 mole of di-*n*-propyl sulfide for 5 hr. at 85–97° to yield 69% of 1-benzoyloxy dipropyl sulfide (II), b.p. 90° at 0.04 mm., n_D^{25} 1.5175, $\gamma_{C=O}$ 1725 cm.$^{-1}$ *Anal.* Calcd. for $C_{13}H_{18}O_2S$: C, 65.53; H, 7.61; S, 13.47; mol. wt., 238. Found: C, 65.59; H, 7.73; S, 13.74; mol. wt., 231. The reaction of 0.3 mole of *t*-butyl peracetate with 0.5 mole of tetrahydrothiophene for 6 hr. at 90° gave 56% of 2-acetoxytetrahydrothiophene (IIIa), b.p. 60–62° at 0.1 mm., n_D^{25} 1.4893, $\gamma_{C=O}$ 1735 cm.$^{-1}$ *Anal.* Calcd. for $C_6H_{10}O_2S$: C, 49.31; H, 6.90; S, 21.90; mol. wt., 146. Found: C, 49.53; H, 7.16; S, 21.86; mol. wt., 141. Also, 0.25 mole of *t*-butyl perbenzoate with 0.5 mole of tetrahydrothiophene for 5 hr. at 90° gave 69% of IIIb, n_D^{25} 1.5650 (after chromatography on alumina), $\gamma_{C=O}$ 1735 cm.$^{-1}$ Because of thermal instability, IIIb could not be purified by distillation. *Anal.* Calcd. for $C_{11}H_{12}O_2S$: C, 63.45; H, 5.81; mol. wt., 208. Found: C, 63.13; H, 6.02; mol. wt., 198.

In the absence of the catalyst the acyloxy compounds formed more slowly and in lesser quantity. Similar to the acyloxy derivatives of ethers, the sulfur compounds are sensitive to heat; they pyrolyze slowly at 100° and rapidly at slightly elevated temperatures. Thus, 2-benzoyloxytetrahydrothiophene (IIIb) at 110° for 2 hr. gave benzoic acid plus an 80% yield of 2,3-dihydrothiophene, b.p. 48° at 100 mm., n_D^{25} 1.5268.[5] *Anal.* Calcd. for C_4H_6S: C, 55.76; H, 7.03; mol. wt., 86. Found: C, 55.41; H, 7.21; mol. wt., 87. After several trap-to-trap distillations the product was shown by vapor phase chromatography to contain less than 1% impurities. Our method constitutes a new and improved synthesis of the 2,3-isomer of dihydrothiophene. When a mixture of IIIb and *t*-butyl alcohol was heated at reflux for about 100 hr., benzoic acid was eliminated quantitatively and an oil was isolated (yield 64%), b.p. 90° at 0.5 mm, n_D^{25} 1.6006. The elemental analyses and the molecular weight agree well with the formula for a dimer of dihydrothiophene. *Anal.* Calcd. for $C_8H_{12}S_2$: C, 55.80; H, 7.03; S, 37.17: mol. wt., 172. Found: C, 55.45; H, 6.77; S, 37.15; mol. wt., 179.

Thermal decomposition of the benzoyloxy derivatives of aliphatic sulfides in the presence of *t*-butyl alcohol gave a different result. Thus, Ib and II gave 1-mercaptoethyl diethyl sulfide and 1-mercaptopropyldipropyl sulfide, respectively.

The observations reported here are being investigated further and the details will be published at a later date.

Acknowledgment. The author is indebted to the Pennsalt Chemical Corporation for a sample of tetrahydrothiophene and to the Phillips Petroleum Company for samples of ethyl and propyl sulfides.

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[2] A brief account of this investigation was presented at the 138th Meeting of the American Chemical Society in New York, N. Y., September 1960.

[3] R. B. Wagner and H. D. Zook, *Synthetic Organic Chemistry*, John Wiley & Son, Inc., New York, N.Y., p. 801, 1953.

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The Free Radical Chemistry of Epoxides: A Radical Rearrangement and Displacement

Sir:

The attack of a free radical or atom on a double bond has long been known,[1] and the corresponding

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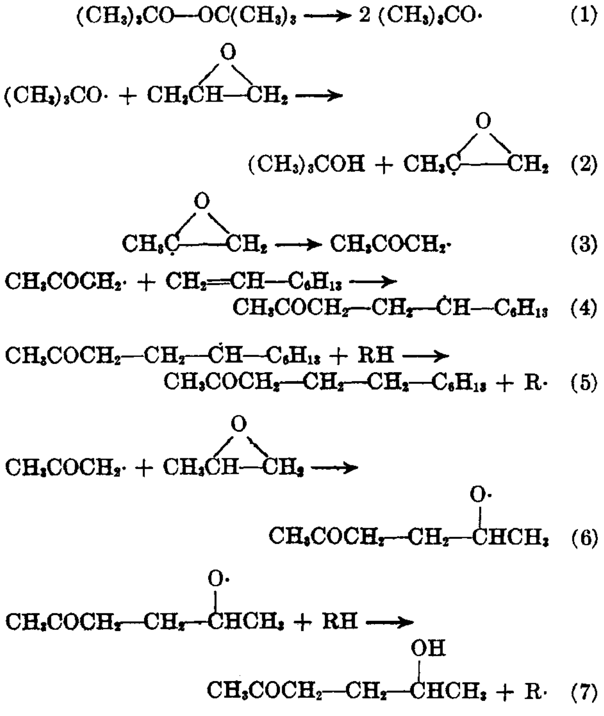
[1] C. Walling, *Free Radicals in Solution*, John Wiley and Sons, Inc., New York, 1957.

attack and ring opening of the three-membered carbon ring has recently been reported.[2] In support of the latter and to report an interesting electron realignment of a free radical, we wish to describe results obtained from a study of the free radical chemistry of the epoxide ring. It was found that the radical formed from propylene oxide by hydrogen atom abstraction isomerized to a keto-radical and that this keto-radical attacked both a double bond and the epoxide ring.

When propylene oxide, 1-octene, and *tert*-butyl peroxide were heated at 150° for 2 hr., a product, b.p. 50–57° (0.26 mm.), was obtained. This was shown to be a 4:1 mixture of 2-undecanone (8.3% yield based on 1-octene) and 5-hydroxy-2-hexanone (2% yield based on propylene oxide) by gas chromatography. When a similar reaction mixture was heated at 125° for 17 hr. the product was mainly the hydroxy ketone. The 2-undecanone gave a semicarbazone, m.p. 118–120°, reported 119–120°,[3] and the 5-hydroxy-2-hexanone was similar to the authentic compound.[4]

The following reaction scheme seems reasonable:



To test the mode of formation of the hydroxy ketone, propylene oxide was brought into reaction with other compounds which have reactive hydrogen atoms. In support of the postulate, toluene, propylene oxide, and *tert*-butyl peroxide gave bibenzyl, 5-hydroxy-2-hexanone, and 4-phenyl-2-butanol; cyclohexane, propylene oxide, and *tert*-butyl peroxide afforded 5-hydroxy-2-hexanone, 2,5-hexanedione, cyclohexylacetone, and 1-cyclohexyl-2-propanol; and ethanol, propylene oxide, and *tert*-butyl peroxide gave 5-hydroxy-2-hexanone and 2,4-pentanediol. All the product identifications were done by gas chromatography by comparison with authentic compounds.

Studies are in progress to determine if the displacement reaction on the epoxide ring (reaction 6) is a frontside or backside attack, and whether or not the *tert*-butoxy radical also gives the displacement.

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[3] H. D. Dakin, *J. Am. Chem. Soc.*, **44**, 47 (1910).

[4] R. M. Adams and C. D. Vanderwerf, *J. Am. Chem. Soc.*, **72**, 4368 (1950).

[5] From the Ph.D. thesis and some post-doctoral research by T. J. W. whose present address is Esso Research and Engineering Co., Linden, N. J.

Photolysis of Aromatic Iodo Compounds as a Synthetic Tool

Sir:

Our interest in the chemistry of thyroxine and related substances[1] led us to examine the photochemical decompositions of certain iodinated thyronines and iodotyrosines. The behavior of these substances, on irradiation, is complex and the interpretation of the results required a prior study of simpler systems. Hence, we studied the photolysis of model substances, such as iodobenzene, *o*- and *p*-iodophenols, *p*-iodonitrobenzene, and 2,6-di-iodo-*p*-cresol under definitive conditions.

Our initial results suggest that photolysis of a variety of iodoaromatic compounds by essentially monochromatic light (2537Å), at or near room temperature, in dilute solution in an appropriate aromatic solvent, is a reaction which has broad synthetic and theoretical implications. While this work was in progress, reports by Szychlinski[2] and Blair and Bryce-Smith,[3] which deal with related reactions, also appeared, but to our knowledge it has not been previously shown that the reactions could be carried out in a synthetically useful manner and with a variety of substituted iodoaryl compounds (*e.g.*, the iodophenols).

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[1] J. Roche, R. Michel, and Walter Wolf, *Bull. soc. Chim. France* 467 (1958); N. Kharasch and N. N. Saha, *Science* **127**, 756 (1958).

[2] J. Szychlinski, *Roczniki Chem.* **34**, 267 (1960).

[3] J. M. Blair and D. Bryce-Smith, *J. Chem. Soc.*, 1788 (1960).